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Preparation and characterization of indium oxide thin films by chemical spray deposition

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Abstract : Conducting and transparent indium oxide thin films are prepared by chemical spray deposition of aqueous solution of indium chloride. X-ray diffraction and optical transmission are used to characterize these films. The preferential orientation of these films is found to be sensitive to deposition parameters. The preparation conditions are optimized to obtain transparent and highly conducting In_2O_3 films on the basis of figure of merit.

Keywords : Spray pyrolysis, semiconductor, indium oxide thin films

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1. Introduction

Transparent conductive indium oxide films have been used extensively in a variety of electronics and optoelectronics applications because of their visible transmittance, high infrared reflectance and low electrical resistivity [1]. In addition to these, indium oxide films have drawn wide applications in fabrication of gas sensors due to the sensitivity of surface conductance to gas adsorption [2]. These films can be deposited by vacuum evaporation [3, 4], sputtering [5], chemical vapour deposition [6] and spray pyrolysis [7]. The spray pyrolysis technique is widely adopted owing to its cost-effectiveness and large area applicability. In the present work, transparent and highly conductive indium oxide thin films were prepared by spray pyrolysis technique.

2. Experimental

Indium oxide films were deposited on heated glass substrates by spraying 0.1 M precursor solution. The precursor solution was prepared by dissolving $InCl_3$ (99.9%) in double distilled deionised water. The optimum deposition parameters, which are summarized in Table 1, are attained by trial and error method. The solution was sprayed onto heated glass substrates held at constant temperature in the range 623-773 K with an accuracy of ± 5 K and the experimental setup is described elsewhere [8]. To enhance the conductivity, the as-deposited films were annealed at 473 K for 45 min under a vacuum of 10^{-5} mbar.

Table 1. Optimum conditions for the spray deposition of In_2O_3 films.

Spray parameter	Optimum value / Suitable item
$InCl_3$ solution concentration	0.1 M
Solvent	Distilled water
Substrate Temperature	723 K
Carrier gas	Compressed Air (2 kg/cm²)
Angular distance	45 ± 1 cm
Rate of spray	6.5 ± 0.1 mL/min
Time of spray	10 min

Characterization of the films was carried out with Philips 1710 X-ray diffraction spectrometer, employing CuKα radiation. The 2θ value is varied from 20 to 70°. Film thickness was measured by Tolansky's interferometric method. The electrical resistivity of the films was measured using four probe technique employed with constant current source and the optical transmission studies using the Shimadzu double beam spectrophotometer UV-240.

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3. Results and discussion

The electrical, optical and structural properties of the thin films have strong dependence on the stoichiometry and microstructure as well as the level of residual stress caused by deposition technique and interaction with the substrate [9]. Fine controls over the spray deposition parameters produce films with smooth and uniform thickness, excellent adherence to the substrates, high visible transmittance and low resistivity. Generally in spray pyrolysis technique, indium oxide on hot surface/atmosphere is formed in principle on reversible endothermic reaction as

$$2InCl_3 + 3H_2O \leftrightarrow In_2O_3 + 6HCl \qquad (1)$$

If these reactions were completed, the resulting indium oxide film would become highly stoichiometric. Since the films obtained by pyrolytic decomposition are conducting, the expected reactions are

$$In_2O_3(s) \leftrightarrow In_2O(g) + O_2(g), \qquad (2)$$

$$In_2O_3(s) \leftrightarrow 2In(g) + 3/2\,O_2(g), \qquad (3)$$

$$In_2O(g) + 2O^{2-} \leftrightarrow In_2O_3(s) + 4e \qquad (4)$$

Alternatively, ionised oxygen vacancies predominate in In_2O_3, according to the defect reaction [10]

$$2In + 3O \leftrightarrow 2In + 3V_o + 6e + 3/2\,O_2 \qquad (5)$$

Hence, the film contains $In_2O_{3-x}(V_0)_x e'_{2x}$ with $x < 0.01$. Here, V_0 denotes the doubly-charged oxygen vacancies and e' denotes the electrons, which are needed for charge neutrality on a macroscopic scale. Thus, the conductivity of In_2O_3 is due to oxygen vacancies that result from incomplete oxidation of the film. These defects are considered to be electron donors. The low resistivity obtained for In_2O_3 films in the present study can be attributed to the above defects.

Another important factor, influencing the film property, is substrate temperature. The variation of thickness with substrate temperature for constant volume of solution sprayed is shown in Figure 1. The thickness of the film may be affected by factors like re evaporation from substrate and enhanced reaction kinetics at higher substrate temperature. From Figure 1, it is evident that the re-evaporation is stronger at higher substrate temperature.

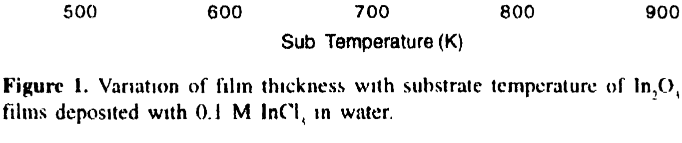

Figure 1. Variation of film thickness with substrate temperature of In_2O_3 films deposited with 0.1 M $InCl_3$ in water.

Figure 2 shows the X-ray diffraction patterns of indium oxide films prepared at different substrate temperatures. All peaks in the diffraction patterns correspond to the cubic structure of In_2O_3 and are indexed on the basis of ASTM card 6-416. All diffractograms of the prepared films clearly indicate the polycrystalline nature of the In_2O_3 films. At 773 K, the preferential orientation is along (400) crystal plane. For deposition temperature below 773 K, the preferential orientation is along (222) plane. Hence, the texture of the film changes from <111> to <100> with increase of substrate temperature. The <100> texture is noticed in films, which are prepared at higher substrate temperature.

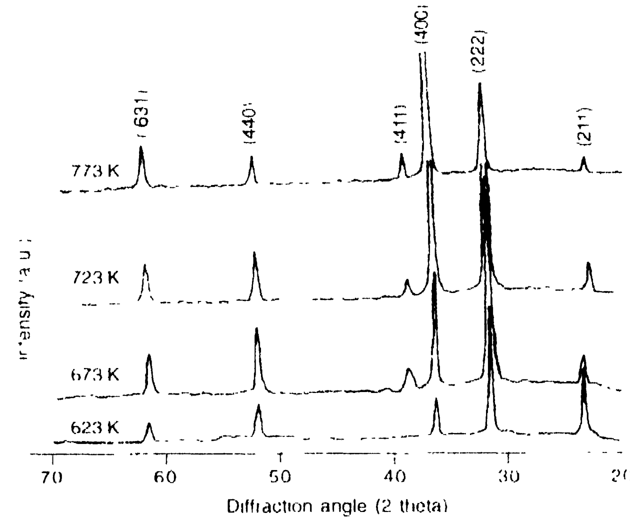

Figure 2. X-ray diffractograms of In_2O_3 films deposited using 0.1M $InCl_3$ aqueous solution at different substrate temperature.

According to Enole and Wirtz [11], in randomly oriented nuclei of In_2O_3, <111> is the fastest growing direction. Here oxygen ion transport is essential in the deposition reaction. This oxygen transport occurs at the time of deposition, but much slowly in In_2O_3 film, once it has been deposited. If the <111> direction grow most rapidly of all possible directions parallel to the substrate, then grains oriented with maximum number of <111> directions in the plane of substrate, should grow most rapidly, at low energy.

In accordance with the mechanism of the film formation, the film growth usually takes place first by nucleation, followed by growth of nuclei and later by coalescence. The nuclei growing on substrates may have various crystallographic orientations coalesce, the resultant crystallite assumes the orientation of the larger one. The most frequent defect is dislocation, which arises at the boundary of two crystal regions that are somewhat angularly displaced with respect to each other. Further, increase in substrate temperature can stimulate oriented growth facilitating crystallization. Any one or more lattice-misfit have taken place here in deposition of In_2O_3 films making preferentially oriented plane sensitive to growth parameters [12].

Figure 3 depicts the optical transmission spectra of the films deposited at different substrate temperatures, from aqueous solution of $InCl_3$. The optical transmission spectra of the films are studied in the wavelength region 300-900 nm. The intrinsic

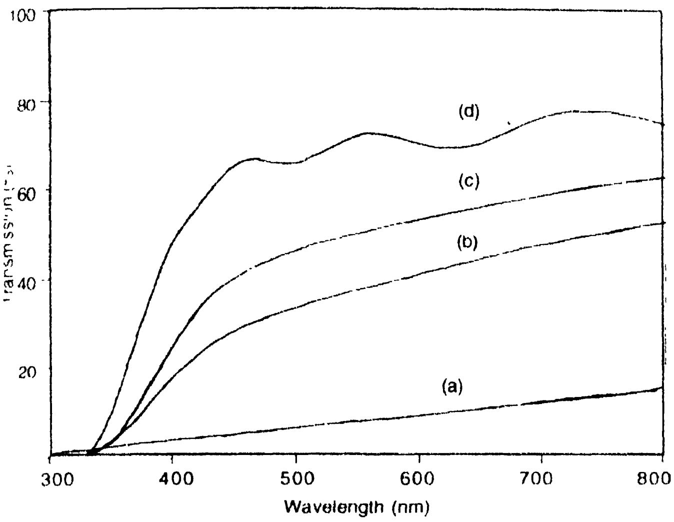

Figure 3. Optical transmission spectra of In_2O_3 films deposited using 0.1M $InCl_3$ solution at (a) 623 (b) 673 (c) 723 and (d) 773 K.

absorption in a semiconductor occurs for wavelength in the vicinity of energy gap. The absorption coefficient α can be calculated from Lambert's formula

$$\alpha = 2.303\, A/d, \tag{6}$$

where A is the optical density and d the thickness of the film. Figure 4 shows the typical variation of the absorption coefficient with photon energy for films deposited at 723 K. The absorption has its minimum at low energy and increases with optical energy

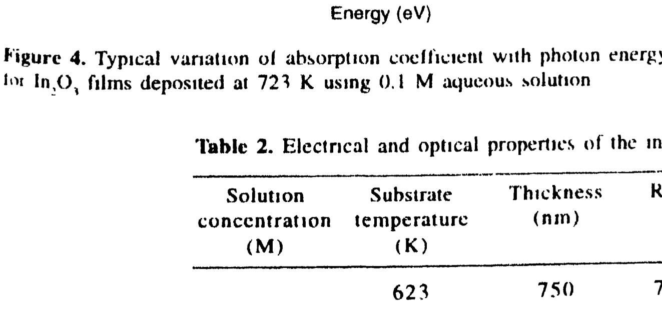

Figure 4. Typical variation of absorption coefficient with photon energy for In_2O_3 films deposited at 723 K using 0.1 M aqueous solution.

in a manner similar to the absorption edge of the semiconductors. It can be seen that these films show high absorption coefficient which is the evidence of direct transition. The absorption curve shows a long wave tail, in the direction of increasing wavelength. This tail might be attributed from stress causing distortion of the crystal lattice or due to the involvement of phonons in the transition [13]. Logarithmic band-edges have been reported for many semiconductors [14] and the phenomena has been explained from diverse models including electric microfields due to ionised defects, thermal fluctuations due to the band-gap and exitonic effects. In the case of In_2O_3, it is reported in the literature that indirect forbidden transitions are known to take place at 2.6 eV [15]. The increase of transmittance with wavelength in the transmission spectrum may be due to the existence of large number of levels in the forbidden gap just below the conduction or just above the valence band. The interference fringes appeared in the transmission spectrum of the film prepared at 773 K. This is the direct evidence of uniform thickness of the film [16], which might arise from the changes in the crystallographic orientations. Assuming that transition become constant at the absorption edge, the absorption coefficient α for directly allowed transitions for simple parabolic scheme can be ascribed as a function of incident photon energy as $\alpha h\nu \propto (h\nu - E_g)^{1/2}$, where E_g is the optical band-gap [17]. Table 2 gives the band-gap values with the deposition temperature for In_2O_3 films using 0.1M $InCl_3$ aqueous solution. Films prepared at critical deposition conditions have the lowest value of band-gap.

Electrical resistivity, transmittance and band-gap of In_2O_3 films deposited from 0.1 M aqueous solution of $InCl_3$ at various substrate temperatures, are presented in Table 2. The resistivity of the as deposited films is very high. This may be due to the grain boundary effects, since the films are of polycrystalline nature. Since, compressed air was used as carrier gas, it is quite likely that a large number of the oxygen molecules are chemisorbed in the film both at the grain boundaries and on the surface. The chemisorption of the oxygen will produce potential barrier, which hinders the electrical transport causing a reduction in conductivity. In order to enhance the conductivity, In_2O_3 films were annealed at 473 K for 45 min under a vacuum of 10^{-5} mbar. On vacuum annealing, the chemisorbed oxygen ions disrobe from the films, donating electrons to it, lowering the resistivity. This is a direct evidence of the existence of an uncontrolled amount of oxygen that acts as electron trap in the

Table 2. Electrical and optical properties of the indium oxide films

Solution concentration (M)	Substrate temperature (K)	Thickness (nm)	Resistivity (Ωm)	Transmission at 550 nm (%)	φ_{TC} (s)	Band-gap (eV)
	623	750	7.5×10^{-3}	10	1×10^{-14}	3.6
	673	720	2.3×10^{-4}	38	2×10^{-7}	3.3
0.1	723	670	7.4×10^{-5}	52	1.3×10^{-5}	3.24
	773	500	1.6×10^{-4}	72	1.22×10^{-4}	3.4

as-deposited samples [10]. This increase in conductivity due to vacuum annealing, can be attributed to increase of carrier concentration and lowering of grain boundary potential. This irreversible change in conductivity is the property causing the modulation in conductivity of the film, when it is placed in a gas atmosphere at an enhanced temperature. The lowest resistivity obtained in the present investigation is 7.4×10^{-5} Ωm deposited at 723 K, which is the critical temperature of In_2O_3 films in the present study. The figure of merit has been a common rating method for indium oxide films using optical transmittance and sheet resistance. Haacke, defined the figure of merit as $\varphi_{TC} = T^{10} / R_{\square}$, where T is the transmittance of the film and $R_{\square}$ is the sheet resistance [18]. The variation of figure of merit of the prepared films with substrate temperature is presented in Table 2.

4. Conclusion

Transparent and conducting indium oxide thin films are prepared by chemical spray deposition of aqueous solution of indium chloride and their deposition conditions are optimized. The films are polycrystalline in nature. The texture of the film is found to change from <111> to <100> with the increase of substrate temperature. The refractive index and band-gap energy of the films prepared under optimum deposition conditions are found as 2.6 and 3.24 eV respectively.

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